APPENDIX C

BRIEF HISTORY OF WASTE STORAGE TANKS AND CHARACTERISTICS OF STORED HIGH-LEVEL LIQUID WASTES

The separations processes began operating in F Area in 1954 and in H Area in 1955, and waste storage was begun immediately. Since that time, 30 waste tanks have been used to contain the 21-million gallons of high-level liquid waste* at the Savannah River Plant. Description of the waste produced in the separations areas, the concentration of this waste in the waste evaporators, and construction of the waste tank facilities can be found in Section II. This Appendix describes the history of waste tanks used and describes the characteristics of the wastes.

WASTE TANK HISTORY

Eight tanks have leaked radioactive waste from the primary tank into the annulus between the primary and secondary tanks. These are Tanks 1, 9, 10, 11, 12, 14, 15 and 16. Of the eight primary tanks that have leaked into the annular space, four have leaked a few gallons each, and only one (Tank 16) has leaked any waste into the surrounding ground, as verified by analyses of ground water samples drawn from wells in the vicinity of the tanks. Locations of ground water monitoring wells from which samples are drawn are shown in Figures III-15, III-16, E-9, and E-10. Inspection procedures and experience used in evaluating tank integrity are discussed in Section II.

F-Area Double-Wall Tanks

Tank 1

The first high-heat waste (HHW)* was received in October 1954. Supernate from this tank was removed in October 1961. The tank was then filled with low-heat waste (LHW).* Its supernate was removed in October 1962 (leaving only the sludge), and the tank was again filled with HHW.

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* The term "high-level-liquid waste," when used in conjunction with waste tank storage at SRP, designates aqueous wastes resulting from the operation of solvent extraction processes. This term includes both "high-heat waste" (HHW) which requires cooling, and "low-heat waste" (LHW) which requires no cooling. This is described further in Section II-A.4.

Supernate was again removed in February and April 1969. The sludge, which had compacted and hardened, was slurried out during two operations in May and August 1969. The final slurrying was preceded by a soaking operation to loosen the consolidated sludge. Addition of concentrate from the evaporator was then begun, and at the present time the tank contains mostly crystallized salts.

A small amount of dried waste salt was observed in the annular space in February 1969. The amount of salt present had not changed in September and November 1975 when detailed inspections were made. Inspections of the observable 30 to 40% of the primary tank wall have failed to reveal the location of the leak(s).

Two of the 36 built-in cooling coils have leaked and have been removed from service by disconnecting and blanking both the inlet and outlet of the coils.

Tank 2

This tank initially received HHW in 1955. Its supernate was removed after about 10 years. The sludge was removed a few months later, and the tank has since been used to store evaporator concentrate. It currently contains mostly crystallized salts.

After the initial sludge had been removed from the tank, it remained empty, except for residual sludge and slurry water, for 14 months during which time 6 of the 36 tank cooling coils began to leak and were removed from service. A leaking section of a cooling coil was removed from the tank for inspection, which showed that the leaks were caused by pitting corrosion along a horizontal line. The position of the corrosion line did not correlate with known interface levels prior to the first coil leak. One additional coil developed a leak in 1968 and was blanked.

There are no known leaks in the primary liner. Ultrasonic measurements of tank wall thickness taken in 1967, 1972, and 1973 showed no detectable decrease in metal thickness.

Tank 3

HHW was the first waste received in this tank in 1956. Supernate was removed after about 12 years of storage. Sludge was removed a year later, and the tank has since been used to store evaporator concentrate. Currently, the tank contains mostly crystallized salts.

There are no known leaks in the primary liner. One cooling coil has leaked.

Tank 4

The first waste received in this tank was HHW in 1961. After 10 years, part of the supernate was removed. Evaporator concentrate was added to the tank to form a high-specific-gravity blend (semiconcentrate*) with the remaining HHW heel. The original batch of semiconcentrate was subsequently transferred from the tank, and the tank was used to receive and age HHW prior to evaporating the supernate.

This tank has no known leaks in the primary liner and no failed cooling coils.

Tank 5

HHW was received in this tank in 1959 and removed after about 7 years. Then the tank was filled with HHW which contained relatively high-chloride (∿0.1 wt %) curium processing waste from the Savannah River Laboratory. After another 5 years, the tank was emptied and has been refilled several times with semiconcentrate. Tank 5 is currently empty and serves as an emergency spare for the F-Area tank farm.

There are no known leaks in the primary liner or cooling coils. In 1967 and 1973 ultrasonic measurements of tank wall thickness showed no detectable loss of metal.

Tank 6

This tank was initially filled with HHW in 1964, and has since been filled several additional times. No known leaks exist in the primary liner, and no cooling coils leak. Wall thickness measurements in 1974 showed no loss of metal. Tank 6 is currently empty and serves as an emergency spare for F Area.

Tank 7

This tank received fresh LHW for several years, starting in 1954, with supernate transferred intermittently to the evaporator feed tank. Then HHW as received, and the tank contained mixtures of HHW and LHW. It also received the sludge removed from Tanks 1, 2, and 3. In recent years, it has contained mostly recycled HHW semiconcentrate.

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* Semiconcentrate is placed in tanks that contain sludge. It is the highest waste concentration from which salts will not crystallize. This prevents possible salt loading on cooling coils and thermowells, which are connected to the tank top.

There are no known leaks in the primary liner, and none of the 36 cooling coils leak. Wall thickness measurements in 1974 showed no loss of metal.

Tank 8

LHW was initially received into this tank in 1956 but after about 4 years it was converted to HHW service. Since being placed in HHW service, it has been filled and emptied several times.

There are no known leaks in the primary liner. One of the 36 cooling coils began leaking in January 1970 and was removed from service. Wall thickness measurements in 1973 showed no loss of metal.

This tank was overfilled in 1961 resulting in a release of radioactive waste to the soil below grade. See Section III, page III-85, for details.

Tanks 25, 26, 27 and 28

These stress-relieved Type III tanks are currently under construction with completion scheduled for October 1978.

Tanks 33 and 34

These tanks were placed in service in 1974 and 1973, respectively. Both tanks are used to receive evaporator concentrate. They originally were without water cooling, but have recently been fitted with 5 and 7 deployable coolers, respectively, and others may be added later. Neither of these tanks have known leaks.

F-Area Single-Wall Tanks

Tank 17

In 1961, dilute LHW was routed into Tank 17 until it was full, and then was allowed to flow into Tank 19 through a cascade line. Later, LHW concentrate from the evaporator was routed into the tank after removal of the dilute LHW. Filling the tank with evaporator LHW concentrate and decanting the cooled liquid supernate for re-evaporation occurred a number of times before the tank was again placed in fresh LHW service. Since that time, the tank has been used to collect fresh LHW. A portion of the LHW salt deposited in Tank 17 while it was in concentrate service has subsequently been dissolved by the unsaturated fresh LHW. This tank has no known leaks.

Tank 18

LHW was routed into Tank 18 in 1959. After about 8 months the tank was placed in service as a feed tank for the evaporator. This service has continued over the years and has included both HHW and LHW; the two types of waste have been segregated and alternated so that HHW concentrate can be stored in double-wall tanks and LHW concentrate, much lower in radioactivity, can be stored in single-wall tanks. This tank has no known leaks.

Tank 19

Initial waste to Tank 19 was dilute LHW in 1961. After this dilute waste was transferred, evaporator concentrate containing both HHW and LHW was allowed to crystallize in this tank. Fresh dilute LHW was added to this tank for over a year, dissolving the HHW salts. Recently only LHW concentrate has been placed in the tank.

Bottom sump samples began to show some radioactivity in July 1973. The source of the contamination was found to be condensate. (See discussion on Tank 21.) The tank has no known leaks.

Tank 20

This tank has been used since 1960 to receive and store evaporator concentrate (primarily LHW but including some HHW). Most of this HHW has been transferred out and routed to double-wall tanks. Currently, Tank 20 is being used for storage of LHW concentrate. No known leaks exist in this tank.

H-Area Double-Wall Tanks

Tank 9

This tank first received HHW in 1955. In 1965, most of the HHW supernate was removed, and in 1966 the sludge was slurried from the tank. Then, HHW concentrate was placed in the tank, and salts were allowed to crystallize. Tank 9 currently contains mostly crystallized salts.

In October 1957, radioactivity was detected at the annulus air exit duct, and it was found that 4 to 5 inches of liquid waste had accumulated in the annular space. A transfer jet was installed to return annulus liquid to the tank. The liquid and salt in the annulus were returned to the tank during an annulus flushing program

between February 1958 and March 1959. The level of liquid waste in the annular space increased to about 12 inches in 1961 and has remained about the same, gradually evaporating to solid salt. Inspections and roddings in 1972 showed about 9 inches of damp salt. Because Tanks 9-12 are located below the water table (Table II-11), any leakage through the concrete encasement structures of these tanks would be ground water leaking into the annulus.

Eight coils developed leaks and were removed from service between February 1965 and August 1967. Six of these followed sludge removal in July 1966.

Tank 10

This tank was put into service receiving HHW in December 1955. HHW supernate was removed from the tank after 12 years, and the sludge was removed by a slurrying operation shortly thereafter. Concentrated HHW from Tank 9 was transferred to Tank 10 in September 1967, and soon thereafter the tank was used as the hot (80 to 100°C), first-stage tank of a two-stage transfer procedure in which evaporator concentrate was collected in Tank 10 and then retransferred to another tank for cooling and crystallization of salts. This mode of operation continued from April 1968 to mid-1971; cooling water was later turned on to the tank cooling coils. The tank currently contains mostly crystallized salts.

Dried waste salt was discovered in the annulus during a visual inspection in July 1959. The dried waste salt indicated probable small self-sealing leaks in the primary tank. Subsequent periodic roddings of the annulus showed no liquid waste until 2 years later, when 1¼ in. was found. During the next 4 years, the liquid level ranged up to 2½ in., but dried to a salt cake by April 1965. Roddings showed up to 2½ in. of liquid in the annulus again in March 1966 during a period of heavy rains, but this dried up within about one week indicating that the liquid source was likely rainwater leaking in from the surface. The annular space currently has an estimated 2 in. of damp salt.

After about 5 months of HHW storage, one cooling coil developed a leak in 1956. Six other cooling coils failed in the first 18 months. During the period 1968-1972 when the tank was being used in high-temperature service with the tank cooling coils valved off, 11 coils failed. Three have failed since February 1972, making a total of 21 coil failures out of 36 installed coils.

Tank 11

Tank 11 received LHW in 1955, and after several years was used for HHW service. Following a sludge removal operation, 18 cooling coils failed within 35 days. Because of the possibility that the coils exposed to the sludge were particularly susceptible to corrosion in the vapor space or at the liquid-air interface, the coils were resubmerged. No additional leaks have occurred. Semiconcentrate has since been stored in Tank 11, and it now receives HHW. In 1969 and 1973, ultrasonic measurements of the tank wall thickness showed no significant loss of metal. In 1974, a single leak site was identified by an accumulation of dried salt high on the primary tank wall. Use of the tank for receipt of fresh HHW is continuing with augmented surveillance.

Tank 12

This tank has been used in HHW service. The supernate has been decanted several times. Ultrasonic measurements of wall thickness made in 1969, 1972, and 1973 showed no significant loss of metal. In 1974 a single leak site was identified by an accumulation of dried salt on the primary tank wall. Until March, 1976, this leak site was about 11 ft below the liquid level in the tank, but the dried salt prevents further leakage. The liquid level was subsequently lowered to 4 ft above the leak site. No coils have failed in Tank 12.

Tank 13

LHW was routed into this tank in 1956, and aged HHW and LHW sludges have also been transferred into this tank. It is now used as the feed tank for aged HHW supernate to the H-Area evaporator.

There are no known leaks in the primary liner of Tank 13, and no leaking cooling coils. Wall thickness measurements, showing no loss of metal, were made in 1974.

Tank 14

Tank 14 was placed in service receiving HHW in September 1957. In May 1959, a small amount of dried waste salt was observed in the annular space, indicating a slow leak in the primary container. The level of leaked waste in the Tank 14 annulus increased to about 8 inches by late 1960 and has increased several more inches since then. This waste consists primarily of dried salt, but some liquid collects when the annulus dehumidification system is turned off.

In June 1965, a transfer jet was installed to return annulus liquid to the primary tank, and LHW was routed into Tank 14. In July-August 1968, supernate was transferred from the tank, and sludge removal was begun in December 1968 to prepare it for salt storage service. Because sludge removal was incomplete due to slurry removal pump failure, the tank was instead used for semi-concentrate storage so that salt would not have to be stored resting on the semisolid sludge. One coil developed a leak in February 1967, and three coils leaked in January 1969, after the attempts at sludge removal and while the tank contained only a few inches of residual slurry water. Two additional coils leaked in June 1969.

A second, smaller transfer jet was installed in the annulus in late 1972 and these transfer jets have been used periodically to transfer liquid from the annulus back into the tank. In December 1972, about 14,000 gallons of waste supernate siphoned from the primary tank to the annulus through the small transfer jet piping, raising the level of waste in the annulus to about 33 in. This incident occurred because the discharge piping from the jet extended about 4 inches below the surface of the supernate in the tank and was not completely emptied of liquid by purging with air after use. Transfer procedures and design of transfer jet piping have been modified to prevent siphoning from primary tanks.

Periscope inspections in January 1972 and January 1973 showed approximately 14 inches of damp salt in the annulus and identified about 50 small leak sites defined by accumulations of salt. Routine analyses of water drawn from wells near Tank 14 (Figure E-10) show no evidence of leakage of radioactivity from the secondary container to the surrounding ground.

Tank 15

The first waste received in this tank was HHW supernate transferred from leaking Tank 16 in 1960. Fresh HHW has also been received. The tank was filled and decanted several times by late 1969. The tank then received HHW supernate and semi-concentrate before being returned to fresh HHW service in 1971.

In April 1972 during periscope inspections of the annulus, two small accumulations of salt were observed near the bottom horizontal weld. In March 1973, additional inspection holes were drilled through the tank roof into the annular space, and inspections through these holes have revealed about 15 leak sites defined by accumulations of salt. No liquid has been observed in the annulus. Routine analyses of water drawn from wells near Tank 15 (Figure E-10) show no evidence of leakage of radioactivity from the secondary container to the surrounding ground. No coil leaks have occurred.

Tank 16

Filling of Tank 16 with HHW was started in 1959. Leakage into the annular space was detected in November 1959. In September 1960, the leakage rate increased to a maximum of 4 gpm, and the liquid level in the annular space rose to about 60 inches, which is the elevation of the top of the secondary container (pan), before installation was completed of a transfer jet to return the liquid to the primary tank.

Samplings of ground water pumped from wells drilled adjacent to the tank (Figure E-10) showed that a very small amount of radioactivity escaped into the ground. During extensive pumping of ground water from the wells, about 6 Ci of ^{137}Cs was found. It is estimated that tens of gallons of waste could have reached the soil and that a range of 10 to 500 Ci of ^{137}Cs leaked into the soil with the waste. In October 1960, part of the supernate was removed from the tank, stopping the leakage from the primary tank.

Periscope inspections in 1961-1962 revealed about 175 individual leak sites, defined by accumulations of salt, mostly in the vicinity of welds. In October 1961 and March 1962, two 5-3/4-inch-diameter samples were cut from the top horizontal seam weld of the Tank 16 wall, about 40 ft apart. Metallurgical examination of the samples indicated that stress corrosion was the most likely cause of the cracks.

In September 1967, after the annulus ventilation air flow had been increased and after a study showed that the previous leakage had occurred while the annulus ventilation was off, LHW was routed into the tank to utilize the remaining freeboard below the metal patches covering the holes cut in the upper wall of the tank. In March 1968 a small seepage was observed into the annulus, but this stopped after the annulus exit air filters were changed to improve the ventilation rate. After removal of the LHW the tank was used to store aged HHW and semiconcentrate.

In January-February 1972, periscope inspections revealed enlarged salt deposits on the tank wall and on the pan floor and also the presence of additional leak sites. The waste was transferred out of the tank (down to a sludge heel) in March 1972 as a first step toward taking the tank out of service. Removal of the waste salt and liquid from the annulus pan is scheduled for 1976, and removal of the sludge and chemical decontamination of the primary tank are planned for 1977 and 1978.

Extensive investigations of the fate of the waste that leaked from the secondary container have led to the conclusion that the radioactivity (primarily ^{137}Cs) has migrated only a few feet from the tank and will have no offsite impact.

Tank 29

This was the first stress-relieved Type III tank (built in 1967-1970) to be placed in service (1971). HHW and LHW concentrate is being placed in this tank for crystallization of salts.

The five reciprocating cooling coil bundles (the first type of insertable cooler designed for salt tanks) in this tank are salt-encrusted, immobilized, and inadequate, and are to be supplemented with deployable coil assemblies through other risers in 1977. Wall thickness measurements show no loss of metal thickness. There are no known leaks in the primary liner.

Tank 30

This tank was placed in brief service in 1974 to receive HHW supernate. It was subsequently emptied (in 1974), and serves as the emergency spare for H-Area. No cooling coils are currently installed in the tank, and there are no known leaks in the primary liner. Wall measurements in 1975 showed no metal loss.

Tank 31

Tank 31 was first used in 1972, and is receiving HHW and LHW concentrate for crystallization of salts. Five non-deployable cooling coils were installed in the tank in 1974-1975, and they will be supplemented with several deployable coolers in 1977. There are no known leaks in the primary liner.

Tank 32

This tank was placed in service receiving fresh HHW in 1971. Five removable cooling coil bundles (non-oscillating) are installed in the tank. There are no known leaks in the primary liner.

Tanks 35, 36, and 37

These stress-relieved Type III tanks are currently under construction, with scheduled completion dates of November 1976, and May and April 1977, respectively. Tank 35 will have removable cooling coil bundles like those in Tank 32; the other two tanks will be provided with permanently installed distributed coils similar in function to the vertical coils in Tanks 1 through 16.

H-Area Single-Wall Tanks

Tank 21

This tank was placed in service in 1961. Since 1963 it has served as an evaporator feed tank and has received LHW and aged HHW supernate. It currently receives fresh LHW directly from the canyon building.

In January 1971, following a rise in the liquid level in the bottom leak detection sump, which normally contains some ground water, samples taken from the sump showed low but sustained concentrations of ^{137}Cs and ^{134}Cs activity. The sump liquid has been removed periodically since that time. In-leakage rate has varied (0-15 gallons per day), but the concentration of radioactivity has remained about the same. Extensive investigations, including ground water analyses, tracer tests, and correlation with environmental and operating data, indicate the source of the contaminated water is condensate from the inner surface of the domed concrete tank top leaking down the interface between the concrete tank wall and the steel liner. The tank continues in service as an evaporator feed tank for LHW, and now also serves as the fresh LHW receiver. The surveillance program will provide a basis for corrective action if warranted. There are no known leaks in the steel liner. Ultrasonic measurements in 1973 of the steel bottom of the liner showed no loss of metal.

Tank 22

The first waste to be transferred into this tank was aged HHW supernate. LHW and HHW concentrates have also been added. Salts and supernate were removed from the tank during 1971 through 1974 by dilution with LHW and transfer to another tank. From May 1974 until April 1976, Tank 22 was the receiver for fresh LHW; it has subsequently received LHW concentrate. There are no known leaks in the steel liner. The thickness of the steel bottom of the liner was measured in 1974 and no loss of metal was indicated.

Tank 23

The first waste received in Tank 23 was dilute LHW (1 to 2 wt % dissolved solids) from the Receiving Basin for Offsite Fuels and the Resin Regeneration Facility. The tank has remained in this service, and also receives evaporator overheads batches which do not meet specifications for discard. There are no known leaks in the steel liner. The bottom steel thickness showed no loss when measured in 1973.

Tank 24

The tank first received LHW concentrate. It has also received HHW concentrate and spent zeolite from the Cesium Removal Column. Low levels of contamination were found in the bottom leak detection sump in April 1973 (see discussion of Tank 21). The HHW concentrate is to be removed from this single-walled tank. There are no known leaks in the steel liner.

CHARACTERISTICS OF HIGH-LEVEL LIQUID WASTE

The range of chemical compositions, properties, and principal constituents of high-level liquid waste were summarized in Section II, Table II-6, -7, and -8. Further details are provided below.

The liquid waste received in the waste tanks is made up of many waste streams from the spent fuel reprocessing plants. A composite high-level liquid waste stream (containing both low-heat and high-heat wastes) is described in this appendix. The chemical composition of the major components of this waste stream is given in Table C-1. Table C-2 shows the concentrations of radionuclides in the waste for irradiated components that have been cooled six months before being reprocessed. Both the chemical and radionuclide composition of the waste changes as the waste ages. The major changes are:

- Radiolytic decomposition of the waste. The major effect of this radiolytic decomposition is the slow reduction in the $NaNO_3$ concentration with an equivalent increase in $NaNO_2$ concentration. After 5 to 10 years, the $NaNO_2$ concentration approaches the residual $NaNO_3$ concentration.

- A slow reduction in the NaOH concentration due to reaction with CO_2 absorbed from air, forming Na_2CO_3. (NaOH is added periodically to waste tanks to maintain its concentration.)

- Decay of radionuclides. Figure C-1 shows the decay of the major radionuclides in this waste.

- Partitioning of the waste into sludge and supernate fractions. The sludge scavenges most of the radionuclides from the supernate as it settles to the bottom of the tank.

The sludge is composed primarily of oxides and hydroxides of manganese, iron, and, to a lesser degree, aluminum. It contains essentially all of the fission products originally in the irradiated fuel except cesium, and essentially all of the actinides. The sludge also contains a significant quantity of mercury. Table C-3 gives the composition of radionuclides in the sludge at 1, 5, and 10 years after irradiation.

The supernate portion of the liquid waste after aging will contain dissolved salts and radioactive cesium. Table C-4 gives the radionuclide composition of the supernate 1, 5, and 10 years after irradiation. This supernate is transferred to an evaporator for dewatering, and the concentrate from the evaporator is transferred to a cooled waste tank where the suspended salts settle. Cooling causes additional salt to crystallize. The supernate is returned to the evaporator for further concentration. This

process is repeated until this portion of the waste has been converted to damp salt cake. The salt produced by evaporation of this aged supernate consists of $NaNO_3$, NaOH, Na_2CO_3, $NaNO_2$, Na_2SO_4, and $NaAl(OH)_4$. The radionuclide concentration in the salt is approximately three times that of the supernate (see Table C-4 for values in the supernate).

TABLE C-1

Chemical Composition of Fresh High-Level Liquid Waste

Constituent	*Concentration, molar*
$NaNO_3$	3.3
$NaNO_2$	<0.2
$NaAl(OH)_4$	0.5
NaOH	1
Na_2CO_3	0.1
Na_2SO_4	0.3
$Fe(OH)_3$	0.07
MnO_2	0.02
$Hg(OH)_2$	0.002
Other Solids	0.13[a]

a. Assuming an average molecular weight of 60.